

PRODUCTION OF HYDROGEN CYANIDE FROM METHANE IN A NITROGEN PLASMA JET

I. Reactive Species Titration; Further Quantitative Studies

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INTRODUCTION

The reaction of methane with a nitrogen plasma to make hydrogen cyanide and acetylene is of considerable interest. Conversions are high enough to be of commercial interest on the one hand,^(1,2) while the formation of HCN in particular proceeds in

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- (1) H. M. Hulburt and M. P. Freeman, Trans. N.Y. Acad. Sci., 2, No. 25, 770 (1963).
 - (2) H. W. Leutner, Ind. Eng. Chem. Process Design Develop., 2, 315 (1963).
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such an interesting and reproducible way that clarification of the details of the reaction should considerably advance the use of the plasma jet in synthetic chemistry, and further might be expected to contribute significantly to basic chemical knowledge.

The formally identical synthesis of HCN from "active nitrogen" and methane has been extensively studied⁽³⁻⁵⁾ for more than a half century. That the systems are

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- (3) K. R. Jennings and J. W. Linnett, Quart. Rev. (London) 12, 116 (1958).
 - (4) G. G. Manella, Chem. Rev. 63, 1 (1963).
 - (5) N. E. V. Evans, G. R. Freeman, and C. A. Winkler, Can. J. Chem. 34, 1271 (1956).
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different is apparent, for the high-voltage discharge is a high excitation device, whereas the plasma jet is thought to be nearly in local thermal equilibrium and hence a low excitation device (spectroscopically speaking intermediate between arc and spark.⁽⁶⁾) Furthermore, the plasma jet experiments are performed at one-half at-

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- (6) F. A. Kovolev and Yu. K. Kvaratskheli, Opt. Spectr., (USSR) (English Transl.), 10, 200 (1961).
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mosphere (as opposed to about 1 torr) and at an average temperature twenty times as high on the absolute scale as room temperature, where the bulk of active nitrogen experiments have been performed. Finally, in the plasma jet the carbonaceous species reacting is evidentially not methane. That is, the products other than HCN are acetylene and higher acetylenes with various degrees of saturation. These are the same products that would form if the jet were, say, argon. It has been shown elsewhere⁽⁷⁾ that the precursors for these products form rapidly compared

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- (7) M. P. Freeman and J. F. Skrivan, A.I.Ch.E. (Am. Inst. Chem. Engrs.) J., 8, 450 (1962).
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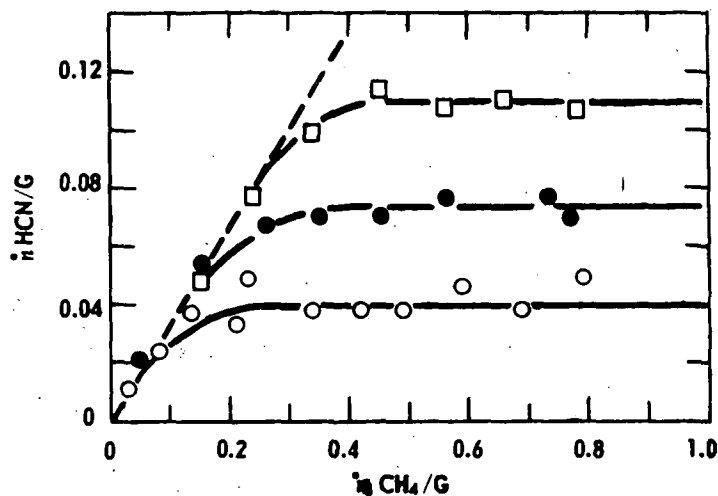
to the time for mixing of the methane with the jet.

There is no question that the plasma jet provides a difficult environment in which to do "good work" in the usual sense. The enormous temperature gradients and consequent inhomogeneities are generally thought of as being a sort of physical chemical bar sinister. On the other hand, perhaps because of their extreme magnitude, the effects due to the temperature gradients are found to be sufficiently reproducible to allow systematic investigation of the jet as a whole, which in its hotter parts represents in a steady state flow situation a chemically unique environment found only in high intensity arc devices. As compensation for tackling this difficult environment, the investigator need not work with trace quantities, but instead with partial pressures and relative conversions at least two orders of magnitude higher than those encountered in active nitrogen research.

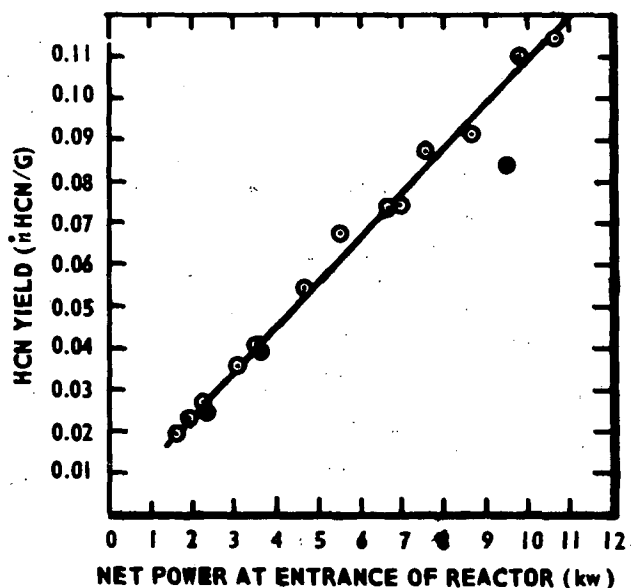
The work reported here represents a systematic continuation of a study performed some time ago.⁽⁸⁾ The procedure followed then as now is to add methane through an an-

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- (8) M. P. Freeman, "The Nature and Quantitative Determination of the Reactive Species In A Nitrogen Plasma Jet," presented at the 147th Natl. Meeting, Amer. Chem. Soc., April 5-10, 1964, Philadelphia, Penn.
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nular slot to a confined nitrogen jet of precisely defined average enthalpy (i.e., a calibrated flow rate and a measured heat flow). It has been shown that under these conditions mixing is very rapid, as is the drop in temperature defined from average enthalpy.⁽⁷⁾ After about one millisecond the resulting flow of high temperature species is further chilled by the entrainment of cold product gas (the fastest of several quench methods investigated on the basis of its efficacy in quenching the ammonia decomposition reaction)⁽⁷⁾ and the flow of HCN in the product gas is chemically determined. Except as noted, the data are taken at 350 ± 20 torr chamber pressure as this pressure is found to reduce the formation of solid product to an insignificant level. As the methane is added at various flow rates the corresponding rate of production of HCN is noted. Just as in e.g., Winkler's work with active nitrogen, a plateau is observed which seems to indicate that some active species is indeed being titrated (Figure 1). Of utmost interest in the older study was the provocatively simple dependence of the plateau level on jet power level (Figure 2). Because this may in turn be shown to correlate with the rate of production of ions in the arc



1. Absolute production rate of HCN vs feed rate of methane (both normalized by dividing by G , the most common flow rate of nitrogen. $G = 0.0171$ g. moles/sec. = 0.383 liter(STP)/sec.) at three net power levels: 3522 watts--o; 6992 watts--o; and 9782 watts--□. Old data, reactor configuration of Figure 5, (0"; 2").



2. Absolute production rate of HCN (normalized) vs net power flowing in gas at entrance to reactor. $CH_4:N_2$: 1: 2. Filled data points were taken at substantially reduced nitrogen flow, 0.0125 g. moles/sec.

process,⁽⁸⁾ it raised the question, still ³³⁵unresolved, as to whether the ions might not in some way be responsible for the chemistry. As a direct consequence there is a long-term quantitative spectroscopic study of plasma jets⁽⁹⁾ currently in progress

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- (9) M. P. Freeman, "A Quantitative Examination of the LTE Condition in the Effluent of an Atmospheric Pressure Argon Plasma Jet," GE-JILA-ONR Symposium on the "Interdisciplinary Aspects of Radiative Energy Transfer," Philadelphia, Penn., Feb. 24-26, 1966. In Press.
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that is expected to ultimately yield information on the nature and quantity of ions, atoms and high temperature molecular species flowing in jets of common plasma materials.

Although thermodynamic calculations had previously been performed for the nitrogen-carbon-hydrogen system⁽¹⁰⁾ they were not in a form easy to compare with plasma

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- (10) C. W. Marynowski, R. C. Phillips, J. C. Phillips, and N. K. Hiester, Ind. Eng. Chem. Fundamentals, 1, 52 (1962).
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jet results obtained under normal operating constraints. The calculations were therefore reproduced⁽¹¹⁾ with the pertinent parameters varied to conform to the exigencies of

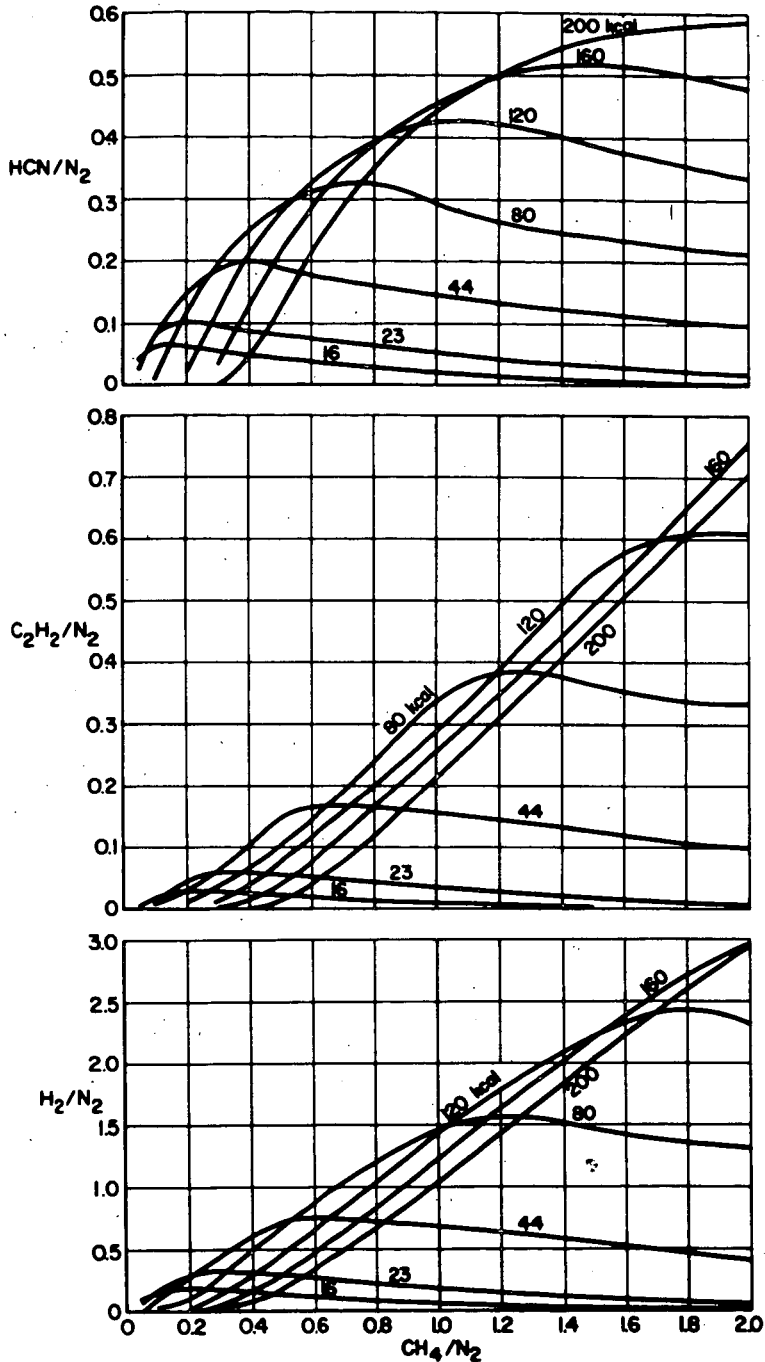
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- (11) B. R. Bronfin, V. N. DiStefano, M. P. Freeman, and R. N. Hazlett, "Thermochemical Equilibrium in the Carbon-Hydrogen-Nitrogen System at Very High Temperatures," Presented at the 15th CIC Chem. Engr. Conf., Quebec City, Quebec, Oct. 25-27, 1965.
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plasma jet operation. Figures 3 and 4 show the results obtained when solid carbon is suppressed in the calculations to be consistent with its absence in the observed products. An important fact immediately emerges. Neither at any experimentally attained average enthalpy, nor at any experimentally used ratio of methane to nitrogen, has the thermodynamically expected yield of HCN for a well-mixed system been exceeded. (Note that the apparent fall-off in calculated yield at high power levels and/or low methane flow rates is due to the competitive formation of cyano, CN, which may be presumed to be an HCN precursor.)

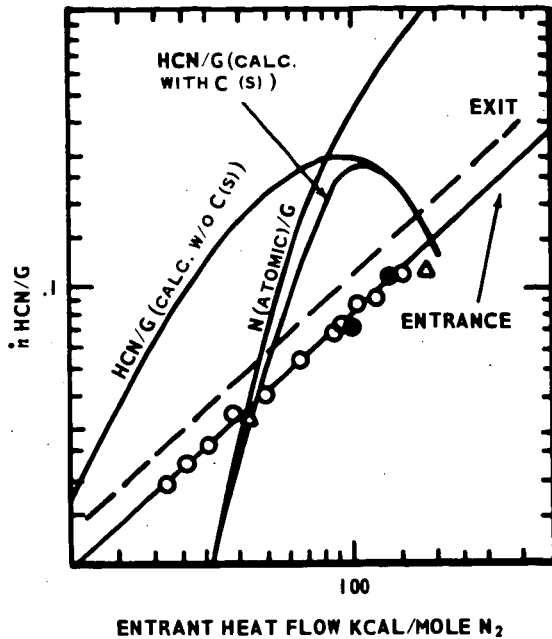
The relationship between the observed and calculated equilibrium yield for the $\text{CH}_4\text{-N}_2$ System is strikingly similar to that recently reported for the F-C-N system by Bronfin⁽¹²⁾ who thereupon advanced the plausible hypothesis that in either case the

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- (12) B. R. Bronfin and R. N. Hazlett, Ind. Eng. Chem. Fundamentals, 5, 472 (1966).
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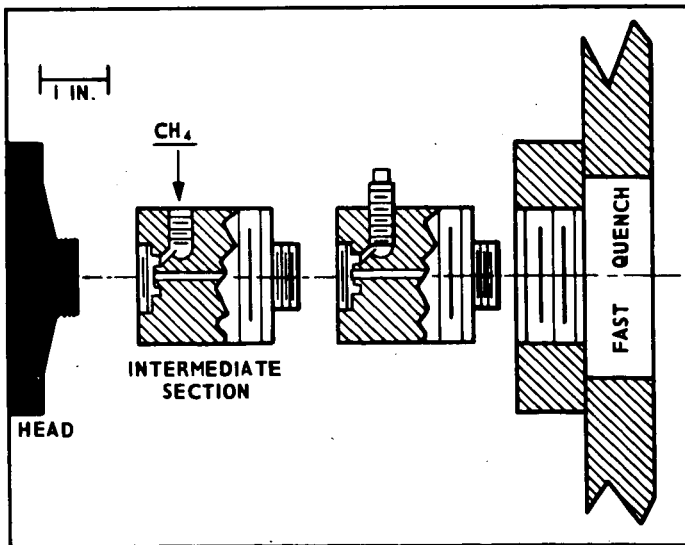
observed yield is in some way a consequence of equilibrium considerations. Now, from earlier work on the acetylene system⁽⁷⁾ it would seem that the composition and



3. Calculated yields of HCN, acetylene and hydrogen relative to initial nitrogen resulting from the indicated nitrogen-methane mixtures. The methane is initially cold and the nitrogen initially at the indicated enthalpy. Solid carbon has been suppressed as a species in this calculation.



4. Old HCN plateau yield data plotted vs initial nitrogen enthalpy. Also shown are the appropriate theoretically calculated curves for HCN (full equilibrium), HCN (carbon suppressed) and N atoms. The dashed line indicates where the somewhat more scattered experimental data would have fallen if plotted vs 2" reactor exit enthalpy.



5. Schematic representation of modular plasma jet reactor showing but two two-inch intermediate sections.

enthalpy dependence are not what one would³³⁸ expect for mixing and subsequent freezing of a reaction in a confining tube and further for the shorter reactors the enthalpy at the exit is still very high. We shall therefore disregard this possibility here. (Note however, that Bronfin is currently testing this model by means of computer

(13) B. R. Bronfin, personal communication.

simulation.) The expected way in which equilibrium could control the reaction is for the product distribution to be a function of the enthalpy and composition profiles at the exit of the reactor where there is an onset of rapid quenching. The calculations indicate that composition is only of secondary importance in the "plateau" region so that presumably the enthalpy profile would be controlling. This differs from true titration in the important respect that in titration one in effect irreversibly consumes a certain potential of the nitrogen jet to form HCN that is clearly a function only of the temperature and/or composition and velocity profile in the nitrogen at the point of mixing but before mixing occurs. If we assume the velocity profile of a plasma jet is uniquely determined by the enthalpy profile,⁽⁹⁾ then the reacting potential as a consequence would in turn be uniquely related to the heat flow in the gas.

Despite this difference, there is no way to distinguish unambiguously between these two possibilities using but one reactor. This is because fractional heat loss from a plasma in a particular reactor type has been shown to be primarily a function of reactor length and arc unit design,⁽¹⁴⁾ so that the ratio of exit heat flow to inlet heat

(14) J. F. Skrivan and W. VonJaskowsky, Ind. Eng. Chem. Process Design Develop. 4, 371 (1965).

flow is nearly constant. The primary objective of the work reported here was therefore to carefully distinguish between these possibilities by performing identical titration experiments in two or more reactors that differ significantly in length in order to determine unambiguously whether inlet or exit heat flow controls the reaction.

It had been inferred from the earlier work by rather incomplete evidence that somehow the capacity to make HCN is primarily dependent on arc conditions no matter how far removed the injection point is from the arc unit itself. A further objective of this experiment was therefore to systematically check this tentative conclusion by careful control and variation of the injection point on a long reactor. From the standpoint of the titration hypothesis, if the arc unit conditions are indeed controlling, then a very long-lived reactive species is implied; such a species is hardly to be expected under these experimental conditions.

Finally, at the same time the older work was being done, Leutner⁽¹⁵⁾ using a very short tubular reactor of otherwise the same design found he was able to work at

(15) H. W. Leutner, Ind. Eng. Chem. Process Design Develop., 2, 315 (1963).

atmospheric pressure and achieve a nitrogen fixation of 12.5% (erroneously reported as 21.9%)(16) in a nitrogen (62%)-argon jet (erroneously reported as pure nitrogen)

(16) C. S. Stokes, personal communication.

with a total flow of 5.0 l(STP)/min. and a power flowing in the gas of 11.5 kw X 55%(16) = 6.32 kw. It was deemed desirable to reproduce his reactor as nearly as possible to attempt to see if the two sets of results were consistent. Such comparison will be made in Part II of this paper, where the effect of argon dilution of the plasma will be discussed in some detail. The contribution such a reactor makes to the present work is of course to extend the range of reactor lengths studied.

EXPERIMENTAL

Apparatus

Plasma-jet reactors consist of three parts, head or arc unit, intermediate section, and quenching section. The plasma-jet heat unit used for this study is a Thermal Dynamics L-40 Plasma-jet with "turbulent nitrogen" electrodes, powered by two 12 kw welding power supplies, open circuit voltage 160 volts, connected in parallel but with opposite phase rotations on their 3 ϕ input so as to minimize line frequency ripple in the output. The intermediate sections (Figure 5) are made of copper and are fully water-cooled, as is the head. The three intermediate sections are themselves modular. Of length 2", 2", and 4", they are mutually compatible and can be joined in any order to make a reactor of length 2, 4, 6, or 8 inches with a feed port at any multiple of 2 inches. Note that the feed rings are not exactly reproducible in that there are residual gaps left when the surrounding gaskets are tightly compressed by the joining threaded parts. The "Leutner reactor" standard Thermal Dynamics spray nozzle with the solids injection port, which is about 1/4" from the nozzle exit, opened up to a 180° slot. The spray nozzle and the turbulent nitrogen electrode used with the intermediate reactors has a 7/32" diameter as do the intermediate reactors. Insofar as the various reactor configurations vary only in length and feed point, it will suffice to distinguish between them with a bracket specifying first the distance from the point of heat balance to the point of methane feed, and second the distance from the point of heat balance to the exit of the reactor. Thus the 8" reactor fed at the 2" point would be designated (2"; 8"), while the Leutner reactor is (-1/4"; 0").

The quenching section where the hot stream of plasma and reaction products are quenched by entrainment of cold product gas is simply a stainless steel pot 11 inches long and 11 inches in diameter sparsely wound with soldered-on copper tubing. All parts subject to heat damage are well-cooled, but between the windings the pot may get hot enough to cause flesh burns. At the outlet of the quenching section is six feet of 1 inch thick rubberized acid hose. This in turn is fastened to the bottom of a vertical mixing section consisting of a three foot long 2" diameter pipe loosely packed with glass wool. The carbon dioxide is mixed with the product stream at the inlet to the mixing section. The top of the mixing section is connected to a high capacity steam vacuum jet with an automatic control valve for maintaining desired pressures.

A Toeppler pump is arranged to withdraw 522 ml of gas from the top of the mixing section at room temperature and at the reactor pressure. This aliquot is then collected for analysis in a suitable gas collection system.

Gas flows except for methane are metered by orifice gages calibrated by water displacement to within 1% for CO_2 and N_2 , respectively. Methane flow, much less critical, is determined by a rotameter calibrated by calculation. All cooling water flows are determined by experimentally calibrated rotameters. Cooling water temperature rise is determined by suitably graduated, interconsistent mercury thermometers.

Procedure

Heat flow in the nitrogen plasma at the point of methane introduction is determined by subtracting from the voltage-current product in the arc the heat lost to all cooling water supplies up to that point. For the most part, just the heat flowing at the exit of the head is required. For data taken at a particular heat flow an attempt is made to keep the heat flow constant. In this endeavor the relatively great intrinsic stability of plasma jets made by this manufacturer help, but especially in runs lasting for several hours it is necessary to continually introduce small corrections. This control is greatly facilitated through use of an analog computer that continuously monitors voltage, current, and cooling water temperature rise and either directly controls the rectifiers or displays the net heat flow in kilowatts continuously on a recorder chart so that manual corrections may be introduced as needed. Heat levels given are generally correct to within $\pm 5\%$.

Except where noted, the pressure in the quenching chamber is kept at 350 ± 20 torr. The actual pressure of each sample is known to ± 1 torr but that is not a significant datum in the analysis and is used only as a consistency check. Quench section pressure measures intermediate section pressures fairly well, but probably not the arc pressures because of the pressure drop through the front orifice of the plasma jet. These arc units are not instrumented to measure the pressure inside the head.

Whenever methane flow rate, power level and/or pressure conditions are changed, the system is operated for eight minutes before taking a sample. This is found to be sufficient time to establish a constant composition.

The collected gas aliquot is slowly bubbled through 200 ml of ice cold-caustic containing 12.5 millimoles of base. The half liter space over the caustic is initially evacuated so that the entire sample, together with the air used to flush the lines, might be collected in the caustic and the space over it. This is followed by one minute of vigorous shaking. This procedure has been found satisfactory for the quantitative recovery of CO_2 and HCN. Total acid in the gas is then determined by back-titration with 0.500 N HCl until all the carbonate has been converted to bicarbonate ($\text{pH} = 8.3$). Ammoniacal KI is then added as an indicator and cyanide determined by precipitometric titration with 0.0100 N silver ion. This permits the initial ratio of HCN to CO_2 to be determined. Because the absolute flow rate of CO_2 is known, the absolute production rate of HCN follows directly. Note that for convenience in presentation the flow rate of HCN is always presented as some fraction of 0.383 l(STP)/sec. (0.0171 gram moles sec⁻¹) so that it may conveniently be compared to the most often used flow rate of nitrogen. In the figures this "standard" flow rate is represented as G.

Accounting for the various sources of uncertainty, the actual HCN flow rate is estimated to be within about 10% of the reported value, and the heat flow to within 5%. Air leakage into the system, a potential source of error, is held below 0.05% of the total gas flow.

The upper limits of operation are fixed by the onset of plugging. For all but the Leutner reactor, solids formation is otherwise negligible though not nonexistent. At high power levels the Leutner reactor does not plug, the heat of the jet evidently serves to clear incipient plugs, but a fair quantity of a low density brown solid is produced that is about 14% polymerized HCN. Its quality is estimated to be small compared to the total methane utilized.

Although temperatures are not quoted, the temperatures corresponding to the extremes of the eight fold average enthalpy range are 3250-7000°K.

Composition Dependence

Figure 6 shows typical "titration" curves for the different situations of interest. In every case a plot of HCN produced vs. methane added (both normalized to the "standard flow rate" of 0.0171 l(STP)/sec) divides cleanly into two regimes separated by a break to which we refer as the "equivalence point." To the left of the equivalence point, the yield is simply dependent on methane feed rate but not on the power level. Lines of slope $1/3$ and $2/3$ are included on the graph to facilitate intercomparison in this region. Although the data are too scattered to draw firm conclusions, it is clear that the break quite generally occurs along the line corresponding to a slope of $1/3$. In this region it is as though the nitrogen were somehow present in excess. To the right of the break the HCN throughput is seen to depend only weakly on methane but, as is demonstrated below, is a strong and simple function of heat flow in the nitrogen before mixing. Excluding for the moment the $(-1/4"; 0")$ data (Figure 6-d), the methane dependence on the right shows a real linear increase with methane flow rate in every case, but this slope is not found to be particularly reproducible since it is apt to change slightly when the apparatus is dismantled and reassembled. Hence the scale has been chosen to emphasize the plateau-like character of the curve. Note that the data excepted may be explained by the fact that in this case the exit rather than the entrant heat flow is regulated. Because of the small heat loss in this short section only a second order effect of this magnitude would be expected.

Power Level Dependence

To take account of the residual slope of the "titration" curves, intercomparison of power-level-dependence studies is done at the same methane flow rate corresponding to one half the "standard" flow whether it is an interpolated point taken from a full titration curve as shown in Figure 6 (filled points) or an isolated measurement (open points). The best line through the old data (Figure 2) appears in Figures 7 through 9 as a reference to aid in intercomparison. Note that Figure 6-a should be exactly consistent with the older data of Figure 1 while the data of Figure 7-b should exactly reproduce Figure 2. The extent that they fail to do this is a fair measure of the nonreproducibility of this experiment when performed in different laboratories, with different equipment, with the chemical analyses performed by different persons.

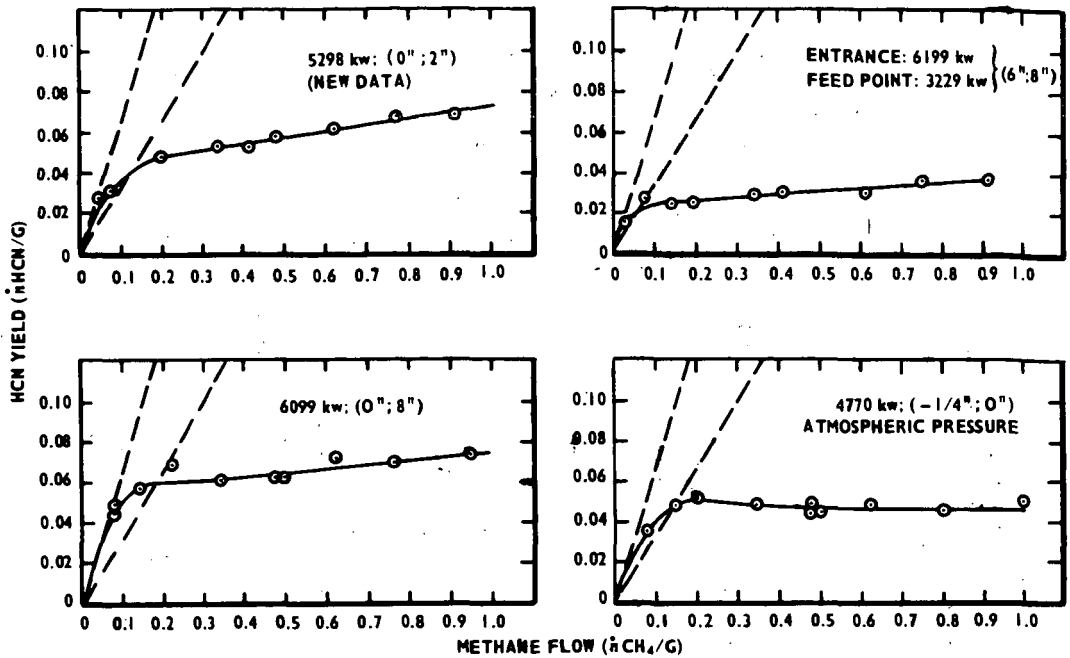
In Figure 7-b data from two different 2" reactors are intermingled as shown. This is to be compared with the $(0"; 8")$ data of Figure 7-a. It is quite clear that within the experimental scatter it would indeed be difficult to improve the agreement. Now the heat leaving the 8" reactor for a given input is only about one half that leaving a 2" reactor for the same input, so that there can be no question but that the HCN production depends only on the heat flow at the point of mixing (or at the exit of the head) and not at all on that at the exit of the reactor.

Mixing Point Dependence

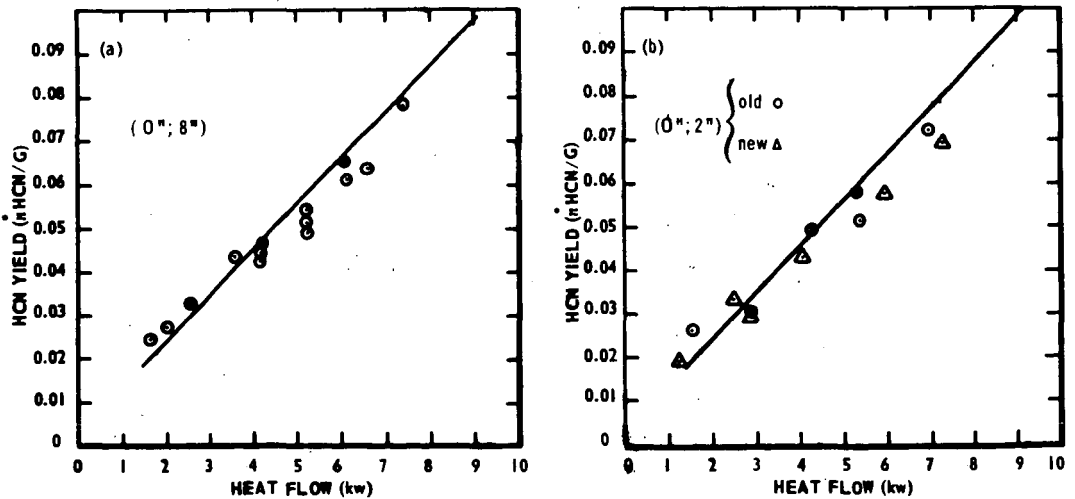
Figure 8 demonstrates clearly that the ability of the nitrogen to make HCN does not persist down the tube at its high initial level, but rather decays as the heat flowing in the gas decays. Shown are a particular set of $(6"; 8")$ data plotted on the left vs heat flow at the exit of the head, and on the right as a function of the heat flowing at the point of mixing, the 6" point. Hence that part of the earlier work indicating the existence of a "long-lived" reactive species is wrong.

Leutner Reactor

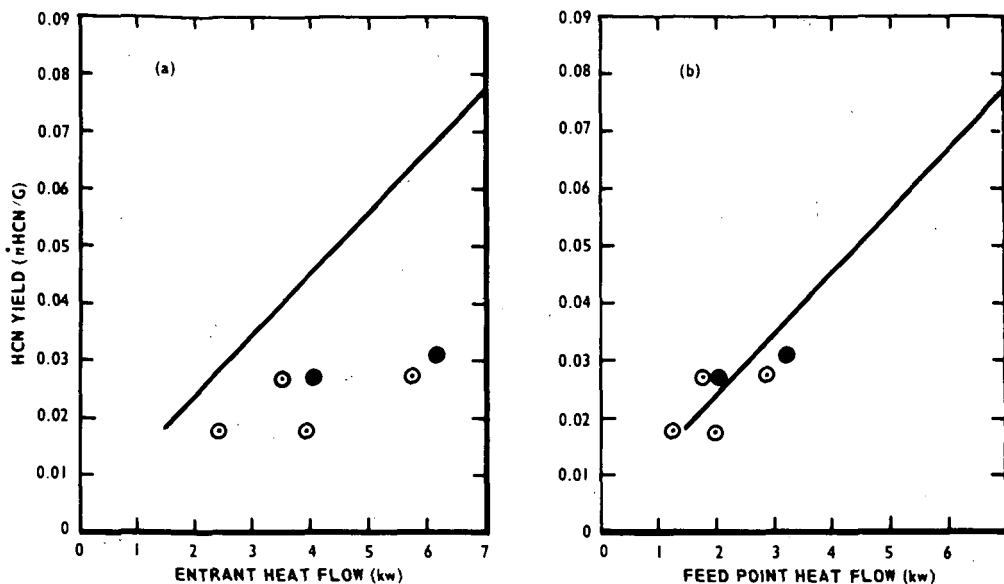
Data for the simulated Leutner reactor are shown in Figure 9. Despite the fact that these data were taken at atmospheric pressure it is clear that the results are completely consistent with those of the other reactors. This agrees with an observation made in the earlier work that there is but slight pressure dependence for this reaction.



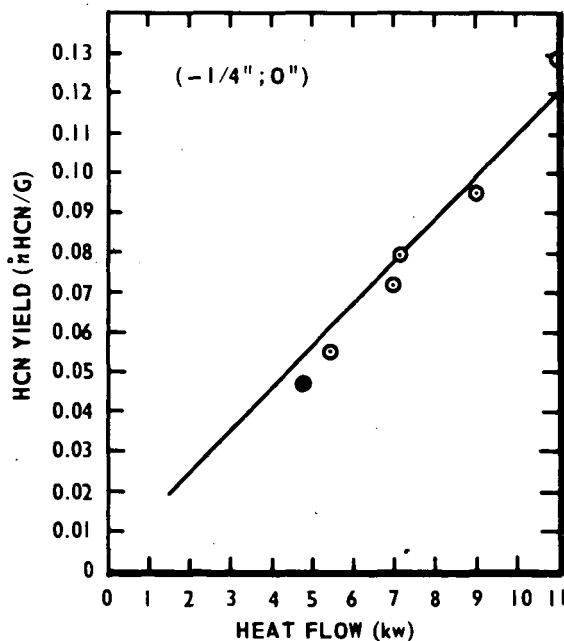
6. Typical titration curves for the case noted. Normalized production rate of HCN vs flow rate of methane. Dashed lines of slope 1/3 and 2/3 are included for reference.



7. Normalized HCN vs heat flow (heat exit power) for the eight inch reactor (left) and the two inch reactor (right). Triangles and circles indicate two different 2" reactors. Filled points were interpolated from full titration curves; open points were isolated runs. The "normal" line of Figure 2 is included in either case for reference.



8. Normalized production rate of HCN for the eight inch reactor fed methane at the six inch point, (6"; 8") data, vs heat flow at (a) the exit of the head and (b) at the 6" feed point. Filled points were interpolated from full titration curves. The "normal" line of Figure 2 is included in either case for reference.



9. Normalized production rate of HCN in the Leutner reactor vs heat flow at the exit of the reactor. The "normal" curve of Figure 2 is included for reference.

Because of the use of diluent argon in his work, comparison with Leutner's results must await Part II of this paper which will explicitly treat this complication. Of significance here is the fact that reactors from 1/4" to 8" in length give the same result, dependent only on entrant heat flow. (Actually for the 1/4" reactor the exit heat flow is measured, but presumably in this case there is a nearly negligible difference.)

Product Distribution

Plateau Region - Mass spectrometer checks made on product formed in the "plateau" region show N_2 , H_2 , HCN, C_2H_2 and CH_4 together with some small quantities of higher acetylenes to be the only species present to any appreciable extent. The N_2 is present of course as a solvent while the H_2 is simply the balance of the hydrogen. The HCN is apparently formed by some sort of irreversible process to be discussed further below while the relative amounts of methane and acetylene seem to conform to considerations investigated previously⁽⁷⁾ for the cracking of methane in an argon jet.

Initial Region - To the left of the break region where the potential of the nitrogen jet to react is in excess, one might expect all of the methane to be converted to HCN, i.e., an initial straight line of unit slope, but such is not the case. Earlier work seemed to favor an initial slope of 1/3 for all titration curves. This would imply that one mole of acetylene is formed for each mole of HCN produced. At the time, however, admittedly crude mass spectrometer checks showed no more than two-thirds to three-quarters mole of acetylene to each mole of HCN. The work reported here indicates an initial slope corresponding to one-quarter to one half mole of acetylene for each mole of HCN. At the breakpoint, however, equimolar quantities of HCN and acetylene would still seem to be the rule. The analytical and sampling apparatuses were neither designed for accuracy nor high precision in this low yield region and it is possible that the differences in the low HCN yield region might have reflected some small change in analytical procedure. It seems more probable, though, that this region is indeed not reproducible and that product distribution here reflects some intangible of the process such as "mixing efficiency", etc. (Note that the reactors are constructed so that the widths of the slots through which the methane flows are not precisely reproducible.)

DISCUSSION

The Titration Curve

It is clear that the reactor length and hence the heat flow at the onset of sudden quenching is irrelevant; the heat flow at the mixing point evidently governs the extent of reaction. It is further seen that the ability of the nitrogen jet to react with the methane decreases as the nitrogen flows down the reactor in such a way that its potential to react with methane, at least with this reactor geometry, is a function only of heat flow in the nitrogen before mixing.

Initial Region - From a different perspective, with no methane flowing in a long tube the reactive potential of the nitrogen jet is seen to persist to some appreciable extent almost indefinitely, but decays as the heat flow decays, presumably through heat conduction processes. As the methane flow is introduced, some of this "potential to react" (PR for brevity) is now used up by the methane, while the balance decays by the heat conduction process. This gives rise to the "initial region."

Equivalence Point - As the methane flow is increased, more of the PR of the nitrogen jet is used by the methane until the equivalence point is reached. At this point none of the PR survives the mixing of the jet with the methane and the break in the curve occurs.

Plateau Region - Because mixing is not instantaneous at the point of mixing, some of the PR is still used up by heat conduction processes at the equivalence point. As the methane flow is further increased, the equivalent amount mixes closer and closer

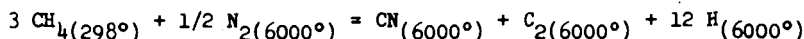
to the slot so that less of the residual ³⁴⁵PR is lost to heat conduction. This latter process probably gives rise to the observed residual slope in the "plateau region" of the titration curves.

The Potential To React

It remains to propose an explanation for the "PR." Although something is being titrated, it is by no means clear just what it is. Nor, as of the present time, has anyone experimentally characterized a nitrogen jet sufficiently well to clearly distinguish between likely alternatives. Nonetheless, it is instructive to examine some of these possibilities for their heuristic value.

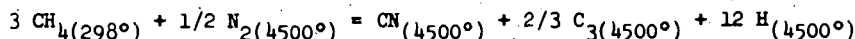
Heat Balance - From Figure 2 a fairly constant heat requirement of 1280 kcal/mole may be obtained. This corresponds very nicely (and probably fortuitously) to the endothermic heat of the most probable reaction at 6000°(17):

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- (17) "Janaf Thermochemical Tables," Dow Chemical Company, Midland, Michigan, December 31, 1960.
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$$\Delta H = 1281 \text{ kcal}$$

or that of the equally probable reaction at 4500°:



$$\Delta H = 1225 \text{ kcal}$$

From this point of view it would appear that the heat of the jet is in some way being titrated by the methane.

Active Species - One might well ask however, if it is just the heat being titrated why does the reaction apparently stop when the core of the jet is still 4000-6000°K? And why is the amount of cyano (CN) formed so sharply limited and constrained so far below the equilibrium value? Note that below 4000° strong exothermic reactions occur that delay further cooling, so that fast quenching cannot be the answer. The most ready answer to these questions is that the HCN reaction is far too slow to equilibrate in jet residence times. Of the manifold complex of forward reaction paths leading to equilibrium, only a few of them will be fast enough to produce HCN in the time available. But these fast reaction paths might well involve nitrogenous species which at thermal equilibrium corresponding to the average enthalpy of the jet, would flow in trace amounts but which, as a consequence of the hot core, are present in the plasma jet at many orders of magnitude higher throughout. Thus we are led naturally to consider this as the titration of some sort of especially reactive species in the jet.

Consider for example a jet producing 0.00171 moles sec⁻¹ of HCN. From Figure 2, we can see that this requires about 9 kv. of heat flowing in the gas. If we assume there is a small core to the jet at 12,000° (enthalpy at one-half atmosphere = 500 kcal/mole),(18) then the heat flow can be accounted for by assuming the hot core occupies

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- (18) F. Martinek, "Thermodynamic and Transport Properties of Gases, Liquid and Solids" McGraw-Hill Book Co., Inc., New York, N.Y., 1959, p. 130.
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about half the diameter of the jet (one fourth the area) and that the nitrogen flowing outside this core carries negligible enthalpy. In this calculation is the unproven assumption carried over from the argon jet⁽⁹⁾ that the mass flux of nitrogen is constant over the entire cross-section. Under the assumed core conditions the jet is 100% dissociated and the atoms 17% ionized. The fluxes are then:

atom flow: $1/4 \times 2 \times (1 - 0.17) \times 0.0171 = 0.0071$ moles sec⁻¹

ion flow: $1/4 \times 2 \times 0.17 \times 0.0171 = 0.00145$ moles sec⁻¹

The ion flow is thus seen to be in excellent agreement with the 0.00171 moles sec⁻¹ production rate of HCN. To some extent this may be due to a fortunate choice of hot core temperature but is nevertheless a promising possibility.

On the other hand there seems to be no good way to account for the reaction on the basis of nitrogen atoms, in this case present in large excess, suggesting that the nitrogen atoms are somehow deactivated before the carbonaceous species enters the hot core. Insofar as the hydrogen from the dissociation of methane must completely fill the reactor in a very short while, it seems probable that the nitrogen atoms are deactivated from this initial infusion, and that the carbonaceous species react with the nitrogen ions (which might well be molecular ions by this time) or some other species sometime later.

CONCLUSION

By systematic variation of reactor geometry it has been conclusively demonstrated that methane added through a peripheral slot to a nitrogen jet titrates, apparently in the true meaning of the word, some potential of the nitrogen jet to react with the thermal decomposition products of methane to form HCN. It is further demonstrated that the potential to react is simply related to heat flow even far down the reactor and is therefore probably the consequence of some steady-state temperature and/or composition profile in a flow with local thermal equilibrium.

For their heuristic value, two superficially different explanations are proposed to explain the "potential to react." On the one hand, the experimental endotherm of the reaction at the equivalence point is shown to be quite consistent with the heat flowing in the hot core of the jet, for a jet model consistent with what we might expect. On the other hand, for the same heat flow and jet model, the yield is shown to be consistent with the flow rate of e.g., ions at the point of mixing and it may equally well be postulated that the ions or some other identifiable species are in fact an active ingredient being titrated.

It is clearly pointless to attempt to conjecture further on the mechanism involved in the titration without more direct evidence on the species and velocity profiles in the jet. A spectroscopic program currently underway in these laboratories will presumably help to fill this gap.

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